

acid either in the gaseous form or in concentrated solution. When heated to 150° it began to darken and exploded at 200°. On the other hand, the nitride obtained by the action of ammonia on selenyl chloride dissolved in benzene begins to darken at a comparatively low temperature and explodes at 130°. When the substance has been carefully purified and is thoroughly dry a slight shock will cause it to detonate violently.

Verneuil¹ in a manner differing but slightly from that of Espenscheid, obtained a similar substance but to which he ascribed the formula Se_3N .

The result of the interaction between ammonia and selenyl chloride in benzene solution evidently depends on the temperature and the concentration of the reacting substances. When the temperature is not too high and the solution is dilute, a highly explosive compound of selenium and nitrogen is formed which has the composition SeN . If, however, a solution of considerable strength be employed, the temperature of the reaction causes the separation of a large quantity of free selenium.

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HYDRONITRIC ACID. VI.

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Anhydrous Hydronitric Acid.

Anhydrous hydronitric acid was first prepared by Curtius and Radenhausen² in 1891. They describe the acid as a colorless, mobile liquid which boils at 37°, and which explodes with great violence when brought into contact with a hot substance. They add that it sometimes explodes spontaneously even at room temperature. They decided to discontinue their investigations because of the explosive character of the compound (Herr Radenhausen was quite seriously injured by one explosion), and they urgently warned others against making further experiments with the anhydrous acid.

It seemed probable, however, that with suitable precautions the operator might be protected from serious injury, and consequently the study of the anhydrous acid was taken up in this laboratory. The devices that were employed to guard against accident are described below; but it may here be stated that, although several violent explosions of the acid occurred during the progress of the investigation, Miss Isham suffered no injury whatever in any case.

¹Bull. soc. chim., 238, 548.

²J. pr. Chem., 43, 207.

The Preparation of Anhydrous Hydronitric Acid, and the Determination of the Melting Point and the Boiling Point of the Compound.

After extended experimentation, the apparatus shown in Fig. 1 was finally adopted for the preparation of the anhydrous acid and for the determination of the melting point and the boiling point of the compound.

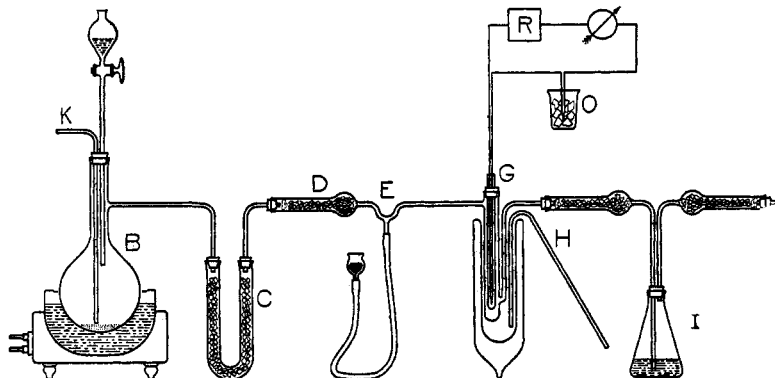


FIG. 1

Dry potassium trinitride was placed in the distilling flask *B*; diluted sulphuric acid (two parts of acid to one part of water, by volume) was slowly dropped upon the salt from the separatory funnel, and air that had been freed from carbon dioxide and moisture was passed into the flask through the glass tube *K*. The hydronitric acid set free was carried along by the current of air through about twelve inches of calcium chloride in the tubes *C* and *D*. It then passed into the receiver, *G*, which itself was placed in an unsilvered Dewar tube. To prevent loss of hydronitric acid that might pass through *G*, without undergoing condensation, the issuing gases were passed through another calcium chloride tube and then into anhydrous methyl alcohol in the flask *I*. This alcohol was protected from the moisture of the air by a second calcium chloride tube. There was also inserted into the Dewar tube a siphon tube *H*.

The whole apparatus was placed in a hood behind a heavy screen of plate glass, and in front of this were placed two wooden screens of pine planks two inches thick, each screen being about six feet high and three feet wide. The edges of these two screens stood about an inch apart and the observations were made through this opening. When handling the anhydrous hydronitric acid, the hands of the operator were always protected by heavy gloves and the eyes by screen goggles of thick plate glass. In addition to these precautions, a small screen of plate glass was always interposed between the face of the operator and the container holding the hydronitric acid.

The temperatures were measured by a pyrometer of iron and constantin, the junctions being soldered and placed in thin-walled glass tubes. One of these tubes (the variable junction) was inserted in the receiver *G*; the other (the ice junction) was immersed in melting ice at *O*. The connection with a sensitive D'Arsonval galvanometer was made through a 20-ohm resistance *R*. The galvanometer was calibrated to temperature readings by placing the ice junction in melting ice and inserting the variable junction, together with an Anschütz thermometer, in a water bath.

In making a determination, the generation of hydronitric acid was begun in *B*, and the Dewar tube surrounding the receiver *G* was filled with liquid air. The acid soon began to condense in *G* above the surface of the liquid air, forming a white, crystalline mass that slowly melted and ran down the sides of the tube as the liquid air evaporated. When sufficient of the acid had collected in the receiver, the mercury level in the small Y-tube *E* was raised, and communication between the receiver and the generating apparatus was thus closed. The pressure in the flask *B* was relieved by breaking the connection with the air intake.

The greater part of the liquid air in the Dewar tube was now driven out by slowly blowing air through the siphon tube *H*. The current of air was then stopped, whereupon the hydronitric acid melted and flowed down to the bottom of the receiver. It was now frozen again by blowing air rapidly through the liquid air still remaining in the Dewar tube. Alternate melting and freezing of the hydronitric acid can be repeated several times by stopping and starting the blast of air. The melting of the frozen acid was observed through a telescope, and at the same time readings were made on the pyrometer. In the first determination of the melting point, the pyrometer readings were not constant, probably because of the smallness of the amount of acid employed. The result first obtained on the pyrometer was 18.8 during the first melting, and after the acid was refrozen, the melting point readings were between 18.5 and 19.5. After the third freezing, the pyrometer stood at 19.7 during the melting.

In the second determination, three grams of potassium triiodide were decomposed, giving about 1.25 grams of anhydrous hydronitric acid. During the melting of this acid, the pyrometer stood quite constant between 19.5 and 19.7, thus indicating a melting point of -80° .

After determining the melting point of a portion of the acid, the boiling point of that same portion was next ascertained by blowing out all of the air from the Dewar tube, allowing the receiver and the Dewar tube to come to room temperature, and then running hot water into the Dewar tube through the siphon tube *H*. The acid was then watched constantly through a telescope to observe when it began to boil, and the galvanometer was read continuously to note when it showed the constant temperature of ebullition. Anhydrous hydronitric acid does not boil freely

under these conditions, but tends to vaporize rapidly from the surface without distinct ebullition. When surrounded by water of a temperature of 70° , the galvanometer rose gradually to 57.3 scale divisions, at which point a bubble rose through the acid, the galvanometer then remaining between 57.3 and 57.5 while the acid vaporized without ebullition. The water in the Dewar tube was then siphoned off, and replaced by water of a temperature of 95° . The galvanometer rose rapidly to 59.2 scale divisions, then dropped to 57.0 as a bubble rose through the acid, and finally stood constant at 57.3. The acid then vaporized rapidly without boiling. To obtain, if possible, definite ebullition, four fine platinum wires, each one inch in length, were placed in the receiver during another experiment. They did not, however, have the desired effect; consequently, they were replaced in a later measurement by a small amount of broken glass, passed through a twenty-mesh sieve. The anhydrous acid was collected and melted as before, and water of a temperature of 95° was then run into the Dewar tube; the galvanometer rose to 58.5; bubbles of gas then appeared in the acid and the galvanometer dropped to 57.6. The acid then exploded, entirely wrecking the apparatus, the decomposition of the compound probably being due to the friction between the sharp pieces of glass when the bubbles rose through them. The temperature corresponding to the mean of the galvanometer readings is about 37° , which is that given by Curtius as the boiling point of the anhydrous acid. This result is probably correct within one-half of one degree.

Properties of Anhydrous Hydronitric Acid.—The acid is a colorless, mobile liquid, heavier than water, and probably of high surface tension and of high vapor tension. It is apparently quite stable at ordinary temperatures. Portions of it have been kept in this laboratory in sealed bulbs for from four to five days without undergoing change. During our experiments with the substance it has never exploded spontaneously, although it explodes readily and with great violence when subjected to shock or when highly heated. The slightness of the shock necessary to effect its decomposition may be seen from the results obtained when the acid was warmed up to its boiling point in contact with broken glass.

To ascertain the character and violence of the explosion of the compound, somewhat more than a gram of it was collected in a receiver that contained a platinum spiral reaching nearly to the bottom of the tube. The spiral was then highly heated by passing through it an electric current. The explosion followed promptly upon closing the circuit, and was accompanied by a sharp, deafening report and a bright flash of light. While the violence of the explosion is very great, its sphere of action is of rather short radius. The iron clamp that held the receiver about four inches above the acid was broken off, and glassware within two feet of

the apparatus was destroyed ; beyond that, however, no damage was done. It was further found that the acid would explode when a flame was held at the mouth of a three-inch tube which contained less than 0.1 gram of the free acid. The acid also explodes when it is heated in a sealed tube to from 60° to 100° and the pressure is suddenly released, or when it is dropped, together with its glass container, upon a hard surface from a height of some feet. In a smooth-walled glass container it is apparently stable at ordinary temperatures, for it has been repeatedly transferred from one to the other of such containers, has been shaken about, and air has been blown through it without an explosion resulting.

Analysis of Anhydrous Hydronitric Acid.—To establish with definiteness that the acid employed in the above experiments was anhydrous, an analysis of the substance became necessary. Although this analysis was fraught with many difficulties because of the very unstable character of the compound, it was carried through to a fairly satisfactory conclusion.

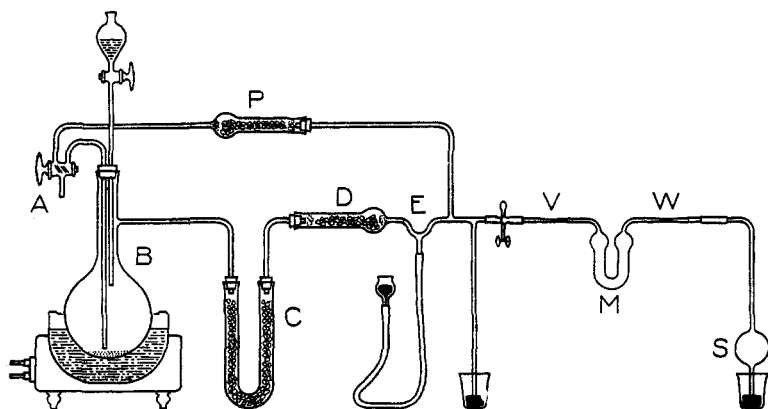


FIG. 2

The procedure was as follows : To the generating apparatus shown in Fig. 1: a branch tube *P* (see Fig. 2), was added, this tube connecting *A* directly to the other side of *E*. This branch contained a drying tube filled with phosphorus pentoxide. A two-way stopcock at *A* made it possible to pass purified air either through the main drying chain or around that chain through the branch tube. Hydronitric acid was generated by the action of dilute sulphuric acid upon potassium trinitride, was dried by the calcium chloride tubes, *C* and *D*, and was condensed in the small U-tube *M* by surrounding that tube with liquid air. This U-tube was connected on its far side to the bulb-tube *S*, the free end of which dipped under mercury. The U-tube *M* was weighed before the evolution of the acid was begun. After sufficient of the acid had collected in the U-tube, the liquid air was removed and the hydronitric acid was

allowed to melt and flow down into the bend of the tube. When such an amount of acid was collected as would leave, after being frozen, some free space above it in the bend of the U-tube, the tube was immersed in liquid air contained in a Dewar goblet and the hydronitric acid was frozen. A current of purified air was then passed through the branch tube *P*, and in this manner the vapor of hydronitric acid in the receiver was driven out. The rubber tube on the entrance side of the receiver was now closed by a pinchcock, and the bulb *S* was gently heated with a Bunsen flame until some of the air was driven out through the mercury. The bulb was then allowed to cool, and the system in this manner was brought under slightly reduced pressure. The U-tube *M*, which throughout this procedure has remained immersed in liquid air up to the small bulbs, was next sealed off at the constriction *V*, and then at *W*. It was allowed to come to room temperature, and was then weighed, as were also the ends that had been sealed off; in this manner the weight of the sample was obtained. The U-tube was then again immersed in liquid air, to reduce the internal pressure, and was connected on one side with a tube supplying a current of pure air, and on the other side with a flask containing a solution of potassium hydroxide. The amount of potassium hydroxide was greater than the amount needed to completely neutralize the acid in the U-tube. The sealed ends of the tubes were broken off inside of the connecting rubber tubing, and the acid was driven over by a current of air into the potassium hydroxide. After all of the hydronitric acid had apparently vaporized, the U-tube was immersed in water of a temperature of about 50°, to insure the complete removal of the condensed acid. The excess of potassium hydroxide in the flask was next carefully neutralized with dilute nitric acid, the hydronitric acid was precipitated with silver nitrate, and the silver trinitride was converted into silver chloride in the usual manner.

Not all of the increase in weight of the U-tube is due to the hydronitric acid condensed in it, but some of the gain results from the increased amount of air in the tube when it is sealed off at the low temperature. The increase in weight due to this cause was approximately ascertained by running a blank with another receiver of the same dimensions as those of the U-tube, this second receiver being weighed, cooled, sealed and again weighed, in exactly the manner employed with the first U-tube. The gain in weight shown by this second tube was subtracted from the weight of the hydronitric acid in the first tube. The results of the two analyses of the anhydrous hydronitric acid by this method are as follows:

	I.	II.
Receiver + HN_3 (sealed) ..	9.6278	8.1813
Receiver empty.....	9.5283	8.0340
	<hr/>	<hr/>
Gain in weight	0.0995	0.1473
Tare sealed.....	10.8812	7.7178
Tare empty.....	10.8764	7.7140
	<hr/>	<hr/>
Gain in weight.....	0.0048	0.0038
Weight of HN_3	0.0947	0.1435
AgCl obtained	0.3140	0.4781
HN_3 calculated.....	0.0944	0.1437
	99.68%	100.2%
Average.....	99.94%	

These results, differing as they do by 0.5 per cent., do not show as close agreement as could be desired ; but when it is remembered that the surface of the glass becomes wet and is dried only by evaporation between two weighings (it was considered unsafe to attempt to dry the glass by wiping it), and also that the conditions under which the tube and its tare were sealed off were probably not identical, the variation in the percentages is probably within the limits of experimental error, and the results suffice to demonstrate that the acid employed in the work was very nearly anhydrous, if not entirely so.

The Vapor Density of Anhydrous Hydronitric Acid.—Mendeleeff,¹ in a paper in which he terms the isolation of hydronitric acid one of the most important discoveries of the year 1890, made three predictions regarding the acid, basing them on its general resemblance to hydrocyanic acid. Since hydrocyanic acid may be regarded as derivable from ammonium formate, hydronitric acid may similarly be considered as derivable from the secondary ammonium salt of the nitrogen acid, $\text{NO}(\text{OH})_3$. This led him to predict—

1. That hydronitric acid would polymerize readily ;
2. That it would form double salts, like the ferrocyanides ;
3. That its ammonium salt would undergo molecular rearrangement from an unsymmetrical to a symmetrical molecule, as ammonium cyanate changes to urea.

The last two predictions have not yet been confirmed. To ascertain whether the acid polymerizes at ordinary temperatures, the authors determined the vapor density of the substance. The determination was made by the Victor Meyer method, which was modified only as regards the weighing of the substance and its introduction into the tube. For the

¹ Ber. 23, 3464.

reception of the samples, small bulbs, with capillary tubes about 8 cm. long, similar to those used in the combustion of volatile liquids, were prepared. These bulbs were weighed empty, and were then filled with anhydrous hydronitric acid by inverting them in the acid, cooling the bulb with a sponge wet with liquid air, turning them into the upright position, freezing the acid with liquid air, sealing the capillary, and weighing again. Several attempts were made to ascertain the vapor density of the acid by placing one of these bulbs of the acid in the Victor Meyer tube, bringing the apparatus to a constant temperature, and then breaking the capillary of the bulb with two glass rods projecting down in the tube and so bent as to act like a pair of shears. In every case the acid exploded when the stem of the bulb was broken, the decomposition of 11 milligrams of the substance being sufficiently violent to pulverize the glass of both the inner and outer tubes of the apparatus. A successful determination was finally made by immersing the weighed and sealed bulb in liquid air until the acid was again frozen, then breaking off the tube and instantly dropping the bulb into the Victor Meyer tube that had already been brought to temperature equilibrium. A bath of boiling chloroform was employed.

0.0223 gram hydronitric acid gave 13.8 cc. gas at 747.6 mm. pressure and 19°, equivalent to 12.4 cc. at 760 mm. pressure and 0°.

	Calculated for HN_3	Found
Molecular weight.....	42.79 (H=2)	40.00
Weight per liter.....	1.923	1.798

This result shows that at a temperature only 25° above the boiling point of the acid, the compound has the molecular formula HN_3 .

CORNELL UNIVERSITY,
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ON SOME PHENOMENA OBSERVED IN THE PEPTIC DIGESTION OF CASEINS.

By J. H. LONG.

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In following up the question of the relation of the casein from cow's milk to that from the goat,¹ I have determined some points in the behavior of the two on treatment with pepsin and very dilute hydrochloric acid. In each experiment I used 10 grams of pure air dry casein made by the Hammarsten method, and mixed with 500 milligrams of a very active specially prepared pepsin, furnished me by Armour & Co., and 1000 cc. of acid containing 2.33 grams of HCl. The mixtures were allowed to undergo digestion at a temperature of 38° in carefully cleaned Bohemian

¹ This Journal, 28, 372.